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FTIR Spectroscopy of Adsorbed Probe Molecules for Analyzing the Surface Properties of Supported Pt (Pd) Catalysts

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1. Introduction

Supported metal catalysts are important for many fields of applied chemistry, including chemical synthesis, petrochemistry, environmental technology, and energy generation/storage. For prediction of catalyst performance in a chosen reaction and optimization of its functions, it is necessary to know the composition of the surface active sites and have methods for estimating their amount and strength. One of the most available and well-developed methods for studying the composition and structure of the surface functional groups of supported metal catalysts is vibrational spectroscopy, in particular with the use of adsorbed probe molecules.

Although Fourier transform infrared (FTIR) spectroscopy is widely employed for characterization of the catalyst surface (Paukshtis, 1992; Ryczkowski, 2001), it is still unclear whether the regularities obtained under conditions of spectral pretreatments and measurements (evacuation, temperature) can be used for interpreting and predicting the surface properties during adsorption of a precursor or in a catalytic reaction. Thus, aim of the present work is not only to demonstrate the possibilities of FTIR spectroscopy of adsorbed molecules for investigation of the surface functional groups in the chosen catalytic systems, but also to compare FTIR spectroscopy data with the data obtained for supported metal catalysts by other physicochemical methods and with the catalyst properties in model and commercially important reactions. Main emphasis will be made on quantitative determination of various surface groups and elucidation of the effect of their ratio on the acid-base, adsorption and catalytic properties of the surface.

The study was performed with model and commercially important supports and catalysts: gamma alumina, which is among the most popular supports in the synthesis of supported metal catalysts for oil refining, petrochemistry, and gas emissions neutralization; supported platinum and palladium catalysts containing sulfated zirconia (Pt/SZ, Pd/SZ) or alumina-

promoted SZ (Pt/SZA), which are suitable for low-temperature isomerization of n-alkanes and hydroisomerization of benzene-containing fractions of gasoline.

2. Vibrational spectroscopy of adsorbed probe molecules for investigation of supported catalysts – Estimation of the strength and concentration of various surface sites

2.1 FTIR spectra of adsorbed probe molecules

FTIR spectroscopy of adsorbed probe molecules is one of the most available and well-developed methods for studying the composition and structure of the surface functional groups of supported metal catalysts. As the vibrational spectrum reflects both the properties of the molecule as a whole and the characteristic features of separate chemical bonds, FTIR spectroscopy offers the fullest possible information on the perturbation experienced by a molecule on contact with the solid surface, and often determines the structure of adsorption complexes and of surface compounds. Examination of supported metal catalysts deals with two types of surfaces strongly differing in their properties: surface of a support and surface of a metal-containing particle. Various species can reside on the support surface: hydroxyl groups of different nature; Lewis acid sites (coordinatively unsaturated surface cations); base sites (bridging oxygen atoms or oxygen atoms of OH groups); structures formed by impurity anions that remain after the synthesis (sulfate, nitrate and ammonia groups) or form upon contacting with air (carbonate-carboxylate structures).

Various spectroscopic probe molecules are widely used for characterization of Lewis and Brønsted acid sites on the surfaces of oxide catalysts. Among such probes are strong bases: amines, ammonia and pyridine, and weak bases: carbon oxide, carbon dioxide and hydrogen (Knözinger, 1976a; Kubelková et al., 1989; Kustov, 1997; Morterra & Magnacca, 1996; Paukshtis, 1992). Being a weaker base than ammonia, pyridine interacts with the sites widely varying in acidity. However, within each type of Lewis acid site, which is determined with pyridine as a probe molecule, there are distinctions in acidity that cannot be revealed with the use of strong bases. In this connection, very advantageous is the adsorption of weak bases like CO. The application of such probe molecules as CO or pyridine makes it possible to estimate both the concentration and the acid strength of OH groups and Lewis acid sites in zeolites, oxide and other systems (Knözinger, 1976b; Paukshtis, 1992). Concentration of the surface groups accessible for identification by FTIR spectroscopy is above 0.1 $\mu\text{mol/g}$.

In the case of base surface sites, the concentration and strength can be characterized with deuteriochloroform (Paukshtis, 1992). Surface of a metal-containing particle may consist of metal atoms with various oxidation states or different charge states caused by the metal-support interaction. Metal cations and atoms on the surface can be detected only from changes in the spectra of adsorbed molecules, since vibrations of the metal-oxygen bonds on the surface belong to the same spectral region as lattice vibrations and thus are not observed in the measurable spectra, whereas vibrational frequencies of the metal-metal bonds are beyond the measuring range of conventional FTIR spectrometers. Surface atoms and nanoparticles of metals and metal ions are usually identified by the method of spectroscopic probe molecules such as CO (Little, 1966; Sheppard & Nguyen, 1978). Examination of the nature of the binding in Me^nCO complexes suggests that the frequency of adsorbed CO (ν_{CO}) should depend on the

valence and coordination states of the cations, that is, on their abilities to accept σ -donation (increasing ν_{CO}) and to donate π -orbitals of the CO (decreasing ν_{CO} , as for carbonyl complexes) (Davydov, 2003; Hadjiivanov & Vayssilov, 2002; Little, 1966). Carbonyls involving π -donation can have different structures – linear or bridged – and the number of metal atoms bonded to the CO molecules can also be different. Complexes involving cations only be linear (terminal) because in an M-O-M situation the distance between cations is too great to form a bond between a CO molecule and two cation sites simultaneously.

2.2 Experimental

The FTIR spectra were measured on a Shimadzu FTIR-8300 spectrometer over a range of 700–6000 cm^{-1} with a resolution of 4 cm^{-1} and 100 scans for signal accumulation. Before spectra recording, powder samples were pressed into thin self-supporting wafers (8–30 mg/cm^2) and activated in a special IR cell under chosen conditions and further in vacuum ($p < 10^{-3}$ mbar). FTIR spectra are presented in the optical density units referred to a catalyst sample weight (g) in 1 cm^2 cross-section of the light flux.

Quantitative measurements in FTIR spectroscopy are based on the empirical Beer–Lambert–Bouguer law interrelating the intensity of light absorption and the concentration of a substance being analyzed. For FTIR spectroscopy of adsorbed molecules, this law is applied in the integral form:

$$A \approx \int \log(T_0/T)_v dv, \quad (1)$$

where A is the integral absorbance (cm^{-1}), T_0 and T are the transmittance along the base line, and the band contour, respectively.

The concentration of active sites on the catalyst surface was estimated by the formula

$$N[\mu\text{mol} / \text{g}] = \frac{A \cdot S}{p \cdot A_0}, \quad (2)$$

where A_0 is the integral absorption coefficient (integral intensity of absorption band (a.b.) for 1 μmol of the adsorbate per 1 cm^2 cross-section of the light flux), p is the weight of a sample wafer (g), and S is the surface area of a sample wafer (cm^2).

The concentration of surface OH groups in $\gamma\text{-Al}_2\text{O}_3$ was determined from the integral intensities of absorption bands ν_{OH} in the region of 3650–3800 cm^{-1} using the integral absorption coefficient $A_0 = 5.3 \text{ cm}/\mu\text{mol}$ (Baumgarten et al., 1989).

In the present study, acidic properties of the samples were examined by FTIR spectroscopy using CO adsorption at -196°C and CO pressure 0.1–10 mbar. An increase in the ν_{CO} band frequency of adsorbed CO relative to the value of free CO molecules (2143 cm^{-1}) is caused by the formation of complexes with Lewis or Brønsted acid sites. Complexes with Lewis acid sites are characterized by the bands with a frequency above 2175 cm^{-1} , whereas the frequency range from 2150 through 2175 cm^{-1} is typical of CO complexes with OH groups.

The concentration of Lewis acid sites was measured by the integral intensity of CO band in the range of 2170–2245 cm^{-1} . For alumina and compositions with prevailing fraction of

alumina (Al_2O_3 and $\text{SO}_4^{2-}\text{-ZrO}_2\text{-Al}_2\text{O}_3$), the following A_0 values ($\text{cm}/\mu\text{mol}$) were used: 1.25 (2245-2220 cm^{-1}), 1.0 (2200 cm^{-1}), 0.9 (2190 and 2178-2180 cm^{-1}); for zirconia and sulfated zirconia, A_0 was equal to 0.8 $\text{cm}/\mu\text{mol}$ (Paukshtis, 1992). A value of the upward ν_{CO} frequency shift determines the strength of Lewis acid sites, as it is related to the heat of complex formation by the following formula (Paukshtis, 1992):

$$Q_{\text{CO}} = 10.5 + 0.5 \cdot (\nu_{\text{CO}} - 2143) \quad (3)$$

The concentration of Brønsted acid sites in the modified aluminum oxides was measured by the integral intensity of CO band in the range of 2170-2175 cm^{-1} , $A_0 = 2.6 \text{ cm}/\mu\text{mol}$. The concentration of Brønsted acid sites in sulfated samples was determined from the integral intensity of absorption band due to the pyridinium ion with a maximum at 1544 cm^{-1} ($A_0 = 3.5 \text{ cm}/\mu\text{mol}$) (Paukshtis, 1992). Adsorption of carbon monoxide on Brønsted acid sites at -196 °C results in the shift of OH bands to the lower frequency region due to perturbation of OH stretch by hydrogen bonding with CO molecule. The higher the shift of OH stretching vibration, the stronger the acidity of this OH group (Maache et al., 1993; Paze et al., 1997).

Basic properties of the samples were studied by FTIR spectroscopy using CDCl_3 adsorption at 20 °C. At the formation of H bonds, deuteriochloroform behaves as a typical acid. A decrease in the frequency of ν_{CD} band of CDCl_3 adsorbed relative to the value of physisorbed molecules (2265 cm^{-1}) is caused by the formation of complexes with base sites. The strength of base site was determined by the band shift of the CD stretching vibrations that occurred under CDCl_3 adsorption. The strength can be recalculated into the proton affinity (PA) scale using the formula (Paukshtis, 1992):

$$\log(\Delta \nu_{\text{CD}}) = 0.0066 \text{ PA} - 4.36 \quad (4)$$

The concentration of base sites was measured by the integral intensity of CD band in the range of 2190-2255 cm^{-1} . The integral absorption coefficient was calculated from the correlation equations (Paukshtis, 1992):

$$A_0 = 0.375 + 0.0158 \Delta \nu_{\text{CD}} \text{ for } \Delta \nu_{\text{CD}} > 13 \text{ cm}^{-1} \quad (5)$$

$$A_0 = 0.125 + 0.0034 \Delta \nu_{\text{CD}} \text{ for } \Delta \nu_{\text{CD}} < 13 \text{ cm}^{-1} \quad (6)$$

3. Investigation of supports and catalysts by FTIR spectroscopy

3.1 Gamma alumina. The role of studying the surface functional groups for understanding the processes of adsorption and catalysis

Owing to its unique acid-base and structural properties, aluminum oxide, first of all $\gamma\text{-Al}_2\text{O}_3$, remains the most popular catalyst and catalyst support. The analysis of catalytic reactions usually deals with Lewis acid and base sites of Al_2O_3 . However, in the catalyst synthesis, adsorption properties of the surface during its interaction with aqueous solutions strongly determine the composition of surface hydroxyl cover of alumina. It should be noted that modern concepts of the surface structure of aluminum oxides, which were developed in recent 50 years, are based mainly on the vibrational spectroscopy data. Various structural models of the aluminum oxide surface were suggested to explain the experimental data

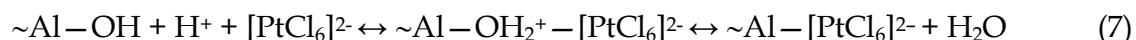
(Egorov, 1961; Peri, 1965; Tsyganenko & Filimonov, 1973; Zamora & Córdoba, 1978; Knözinger & Ratnasamy, 1978). These models are based on the spinel structure of transitional alumina modifications. Recent attempts to develop advanced models of the surface structure or refine the existing models were made by Tsyganenko and Mardilovich (Tsyganenko & Mardilovich, 1996) as well as Liu and Truitt (Liu & Truitt, 1997). Such advanced models admit the existence of fragments on the alumina surface, which comprise pentacoordinated aluminum atom.

At present, 7 absorption bands characterizing the isolated OH groups are commonly distinguished in FTIR spectrum of γ -Al₂O₃. Low-frequency bands are assigned to the bridging OH groups located between aluminum atoms with different coordination: 3665-3675 (Al^{IV}(OH)Al^{IV}), 3685-3690 cm⁻¹ (Al^{VI}(OH)Al^{IV}), 3700-3710 cm⁻¹ (Al^{VI}(OH)Al^V), and 3730-3740 (Al^{VI}(OH)Al^{VI})¹. High-frequency bands correspond to the terminal OH groups bound to one aluminum atom with different coordination: 3745-3758 (Al^VOH), 3765-3776 (Al^{IV}OH), and 3785-3792 (Al^{IV}OH) cm⁻¹. In addition, there is a broad a.b. at 3600 cm⁻¹ attributed to hydrogen-bonded OH groups (Paukshtis, 1992).

The surface Lewis acidity is formed by electron-acceptor sites represented by coordinatively unsaturated aluminum cations on the Al₂O₃ surface. The use of CO as a probe molecule makes it possible to estimate both the strength and the amount of Lewis acid sites, which is essential when alumina is employed as a catalyst or catalyst support. CO is adsorbed on the γ -Al₂O₃ surface to form three types of surface complexes (Della Gatta et al., 1976; Zaki & Knözinger, 1987; Zecchina et al., 1987). FTIR spectra of adsorbed CO show the following a.b. corresponding to stretching vibrations of CO molecule: 2180-2205 cm⁻¹ (weak Lewis acid sites), 2205-2220 cm⁻¹ (medium strength Lewis acid sites), and 2220-2245 cm⁻¹ (strong Lewis acid sites). The high-frequency bands are related with two types of Lewis acid sites including Al^{IV} ions located in configurations with crystallographic defects. The low-frequency bands correspond to Al^{VI} ions in the regular defects of low-index faces of crystallites.

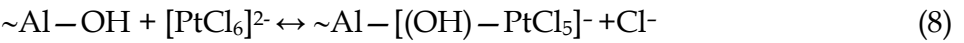
3.1.1 FTIR spectroscopy for determining the sites of precursor anchoring during synthesis of Pt/Al₂O₃ catalysts

In the synthesis of supported platinum catalysts, chloride complexes of platinum (IV) are commonly used as precursors. Their sorption on the alumina surface occurs from aqueous solutions and implies the involvement of OH groups of the support surface. Therewith, two main mechanisms of the interaction between metal complex and support are considered, implementation of each mechanism depending both on the chemical composition of a complex (degree of hydrolysis) and the ratio of various OH groups (Belskaya et al., 2008, 2011; Bourikas, 2006; Lycourghiotis, 2009). The first mechanism consists in the formation of outer sphere complexes; it implies electrostatic interaction between chloroplatinate and alumina surface, which is protonated and positively charged at low pH of the solution:



¹Al^{IV}, Al^V and Al^{VI} are aluminum atoms in tetrahedral, pentahedral and octahedral coordination, respectively

The formation of inner sphere complexes is accompanied by a deeper interaction of a complex with the oxide surface via ligand exchange with the surface OH groups:



FTIR spectroscopy is widely used to investigate state of the surface at different stages of catalyst synthesis. When studying the precursor-support interaction, this method allows identification of OH groups involved in chemisorption of the metal complex. Analysis of

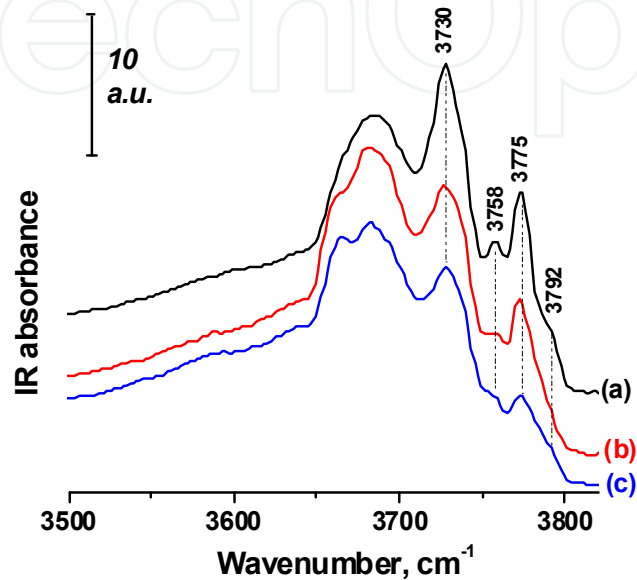


Fig. 1. FTIR spectra of surface hydroxyl groups of $\gamma\text{-Al}_2\text{O}_3$ (a), 0.5% Pt/ $\gamma\text{-Al}_2\text{O}_3$ (b) and 1% Pt/ $\gamma\text{-Al}_2\text{O}_3$ (c). The samples were calcined and outgassed at 500 °C

Sample		$\gamma\text{-Al}_2\text{O}_3$	0.5%Pt/ $\gamma\text{-Al}_2\text{O}_3$	1%Pt/ $\gamma\text{-Al}_2\text{O}_3$	$\gamma\text{-Al}_2\text{O}_3$ Hydrothermal treatment 180 °C, 3 h
Type of OH group					
$\text{Al}^{\text{IV}}\text{OH}$ (3790-3795 cm^{-1})	Concentration, $\mu\text{mol/g}$	12	9	8	6
$\text{Al}^{\text{V}}\text{OH}$ (3775 cm^{-1})		35	29	16	33
$\text{Al}^{\text{VI}}\text{OH}$ (3758 cm^{-1})		34	27	20	28
$\text{Al}^{\text{VI}}(\text{OH})\text{Al}^{\text{VI}}$ (3730-3740 cm^{-1})		107	96	78	89
$\text{Al}^{\text{V}}(\text{OH})\text{Al}^{\text{VI}}$ (3705-3710 cm^{-1})		50	54	52	52
$\text{Al}^{\text{VI}}(\text{OH})\text{Al}^{\text{IV}}$ (3690 cm^{-1})		62	75	67	62
$\text{Al}^{\text{V}}(\text{OH})\text{Al}^{\text{IV}}$ (3665-3670 cm^{-1})		36	35	34	43
$\Sigma \text{ OH}$		336	325	275	313

Table 1. Types and concentrations of hydroxyl groups in calcined alumina and Pt/alumina samples as determined by FTIR spectroscopy data

experimental data presented in Fig. 1 and Table 1 shows that adsorption of platinum complexes followed by anchoring of oxide platinum species forming on the γ -Al₂O₃ surface decreases the intensity only of high-frequency bands. As the amount of supported platinum species increases (platinum content of 0.5 and 1.0 wt%), the concentration of all types of terminal groups (Al^{IV}OH, Al^{VI}OH, Al^{IV}OH) decreases; so does the concentration of bridging OH groups Al^{VI}(OH)Al^{VI} bonded to octahedral aluminum. Exactly these types of OH groups seem to be involved in anchoring the anionic complexes of platinum (IV). Having more strong base properties, they are capable of interacting with chloroplatinate by mechanism (8), acting as the attacking ligand. However, the bridging groups with a.b. 3665-3710 cm⁻¹ (Al^{VI}(OH)Al^{IV}, Al^{IV}(OH)Al^{IV}, Al^{VI}(OH)Al^V) are virtually not involved in platinum anchoring (Table 1).

According to analysis of the spectra of adsorbed CO, in the region of CO stretching vibrations all the samples have a.b. at 2245 and 2238 cm⁻¹ characterizing CO complexes with strong Lewis acid sites, absorption bands at 2220 and 2205 cm⁻¹ characterizing CO complexes with medium strength Lewis acid sites, and absorption bands at 2189-2191 cm⁻¹ characterizing CO complex with weak Lewis acid sites. Deposition of platinum raises the concentration of nearly all types of Lewis acid sites, which is related with introduction of Cl⁻ ion of the complex. Along with this, a substantial decrease in the concentration of weak Lewis acid sites is observed (Table 2). These electron-deficient sites may also take part in the anchoring of anionic platinum complexes via electrostatic interaction (Kwak et al., 2009; Mei et al., 2010).

Type of Lewis acid site	Super strong	Strong	Medium I	Medium II	Weak
ν_{CO} , cm ⁻¹	2245	2238	2220	2205	2189-2191
Q _{CO} , kJ/mol	61.5	58	48.5	41.5	34
Samples	Concentration, $\mu\text{mol/g}$				
γ -Al ₂ O ₃	0.9	2.5	5	9	460
1% Pt/ γ -Al ₂ O ₃	1.2	2.9	6	27	380
γ -Al ₂ O ₃ Hydrothermal treatment 180 °C, 3 h	1.1	4.2	5	24	470

Table 2. Types and concentrations of Lewis acid sites according to FTIR spectroscopy of adsorbed CO

Thus, the analysis of FTIR spectra of alumina provides data on the nature and amount of various surface sites; moreover, it allows identification of the sites where active component precursor is anchored during catalyst synthesis, and makes it possible to hypothesize about mechanism and strength of the metal complex-support interaction.

3.1.2 Novel approaches to varying the composition of surface functional groups of alumina

Variation of the acid-base properties of alumina surface is commonly performed by chemical modifying via the introduction of additional anions (halogens, sulfates, phosphates) or cations (alkaline or alkaline earth metals) (Bocanegra et al., 2006; Ghosh & Kydd, 1985; Lisboa et al., 2005; López Cordero et al., 1989; Marceau et al., 1996; Requies et

al., 2006; Rombi et al., 2003; Scokart et al., 1979; Wang et al., 1994). These methods complicate the process of catalyst synthesis and can lead to non-reproducible results.

This Section presents some unconventional approaches to alumina modifying for controlling the state of its surface functional cover. One of approaches consists in altering the relative content of hydroxyl groups and Lewis acid sites on the γ - Al_2O_3 surface without changes in the chemical composition of support (Mironenko et al., 2009, 2011). For this purpose, two techniques are employed: chemisorption of aluminum oxalate complexes followed by their thermal decomposition, and hydrothermal treatment of γ - Al_2O_3 . Besides, there is an approach leading to considerable enhancement of acidic properties of the surface. Such effect is provided by γ - Al_2O_3 promotion with silica. The formation of SiO_2 takes place in the pore space of alumina during thermal decomposition of preliminarily introduced silicon-containing precursor.

3.1.2.1 Modifying the functional cover of the γ - Al_2O_3 surface using aluminum oxalate complexes

The proposed method of modifying implies the chemisorption (in distinction to conventional methods of incipient wetness impregnation) of anionic aluminum oxalate complexes $[\text{Al}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]^-$ and $[\text{Al}(\text{C}_2\text{O}_4)_3]^{3-}$ on the γ - Al_2O_3 surface. It is essential that this approach excludes both the formation of a bulk alumina phase in the porous space after decomposition of supported complexes, and considerable changes in the texture parameters. Analysis of FTIR spectra of the modified alumina surface hydroxyl cover revealed (Fig. 2) that chemisorption of the oxalate complexes and subsequent formation of aluminum oxide compounds supported on γ - Al_2O_3 (calcination at 550 °C) decreased mainly the intensity of two a.b. at 3670 and 3775 cm^{-1} . These bands characterize the bridging and terminal OH groups bound to pentacoordinated aluminum atom. Probably these are exactly the groups that are involved in anchoring of aluminum oxalate complexes.

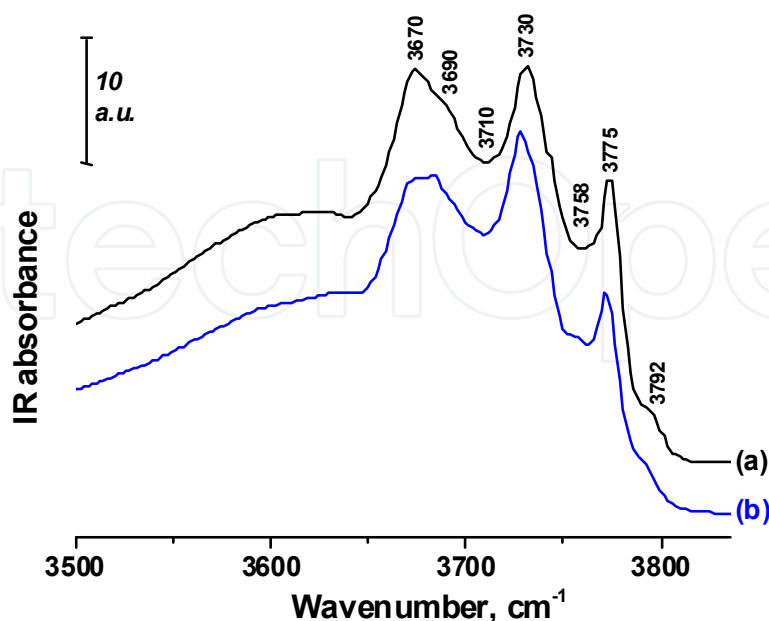


Fig. 2. FTIR spectra of surface hydroxyl groups of γ - Al_2O_3 (a) and 3% $\text{Al}_2\text{O}_3/\gamma$ - Al_2O_3 (b). The samples were calcined and outgassed at 500 °C

However, the formation of aluminum oxide compounds having their own surface OH groups ($\text{Al}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$) resulted in substantial changes in the adsorption and acidic properties of the $\gamma\text{-Al}_2\text{O}_3$ surface. Thus, investigation of the sorption of chloride complexes of platinum (IV) on the modified $\gamma\text{-Al}_2\text{O}_3$ showed a 1.5-fold increase in the sorption capacity and an increased strength of the metal complex-support interaction (Mironenko et al., 2009).

According to FTIR spectroscopy of adsorbed CO (Fig. 3, Table 3), the anchoring of aluminum oxide compounds on the surface of initial $\gamma\text{-Al}_2\text{O}_3$ support decreased the concentration of weak Lewis acid sites with a.b. $\nu_{\text{CO}} = 2191\text{ cm}^{-1}$ (regular defects of the alumina surface including the octahedral aluminum ion) without changes in the concentration of other types of Lewis acid sites.

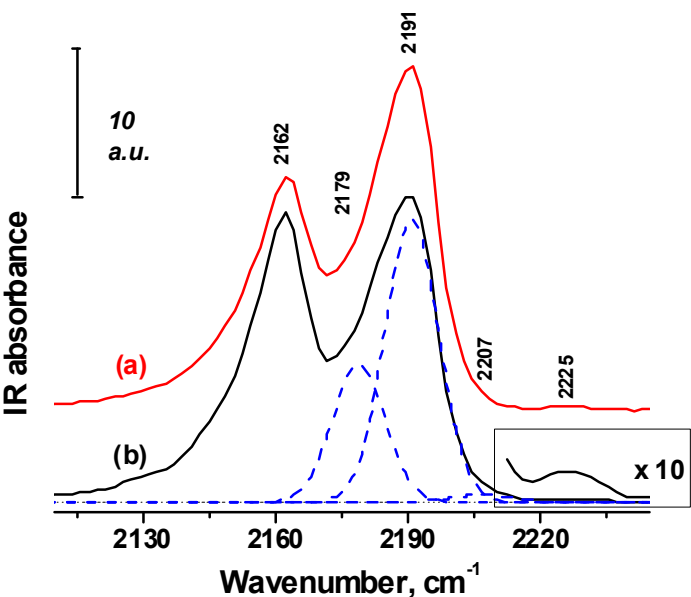


Fig. 3. FTIR spectra of CO adsorbed at $-196\text{ }^{\circ}\text{C}$ and a CO pressure of 4 mbar: (a) $\gamma\text{-Al}_2\text{O}_3$, (b) $3\%\text{Al}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$. The dashed line shows the deconvolution of spectrum (b) into its components. Inset: portion of spectrum (b) magnified 10 times

Sample	Lewis acid site concentration, $\mu\text{mol/g}$				
	2179 cm^{-1}	2191 cm^{-1}	2207 cm^{-1}	2225 cm^{-1}	Σ
$\gamma\text{-Al}_2\text{O}_3$	155	360	8	3	526
$3\%\text{Al}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$	155	330	7	2	494

Table 3. Concentrations of Lewis acid sites characterized by different absorption bands in the FTIR spectrum of adsorbed CO

A decrease in the surface acidity revealed by FTIR spectroscopy of adsorbed CO is in good agreement with the results of catalytic testing (Fig. 4). Alumina samples before and after modifying were compared in a model reaction of 1-hexene double-bond isomerization, which is sensitive to amount and strength of Lewis acid sites. Although the reaction conditions radically differ from conditions of spectral measurements, the observed decrease in 1-hexene conversion can be predicted and interpreted using FTIR spectroscopy data.

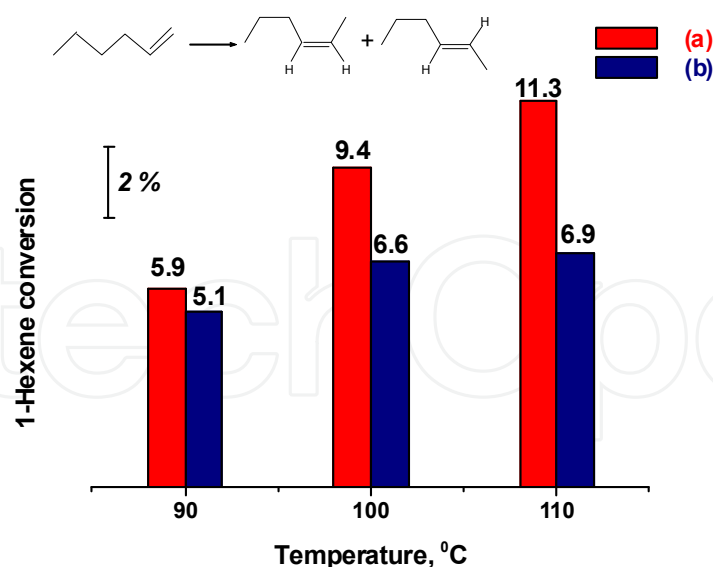


Fig. 4. Temperature dependence of the 1-hexene conversion: (a) γ -Al₂O₃, (b) 3% Al₂O₃/ γ -Al₂O₃. Reaction conditions: atmospheric pressure, T = 90-110 °C, He : C₆H₁₂ molar ratio 3.3

3.1.2.2 Modifying the functional cover of the γ -Al₂O₃ surface at hydrothermal treatment

Hydrothermal treatment of γ -Al₂O₃ is commonly used for alteration of the porous structure parameters (Chertov et al., 1982). Our study demonstrated that this technique is efficient for controlling the state of the oxide surface. Hydrothermal treatment of γ -Al₂O₃ was carried out in a temperature range of 50-200 °C with the treatment time varying from 0.5 to 12 h. This produced a hydroxide phase of boehmite AlO(OH) on the γ -Al₂O₃ surface, which amount can be readily controlled by the treatment conditions. After hydrothermal treatment, the samples were calcined at 550 °C to reduce the oxide phase.

The FTIR spectroscopic examination revealed the hydrothermal treatment effect on the concentration and ratio of functional groups on the γ -Al₂O₃ surface. Figure 5 shows FTIR spectra of the surface hydroxyl cover of initial γ -Al₂O₃ and γ -Al₂O₃ subjected to hydrothermal treatment at various temperatures with subsequent calcination at 550 °C. The quantitative analysis of FTIR spectroscopy data (Fig. 5 and Table 1) showed changes in the relative content of different surface OH groups of γ -Al₂O₃ with elevation of hydrothermal treatment temperature. This modifying technique was found to increase the fraction of low-frequency bridging hydroxyl groups ($\nu_{\text{OH}} = 3710\text{-}3670\text{ cm}^{-1}$) from 50 to 70% of all OH groups and decrease the content of terminal hydroxyl groups ($\nu_{\text{OH}} = 3790\text{-}3760\text{ cm}^{-1}$) and especially the bridging group Al^{VI}(OH)Al^{VI} ($\nu_{\text{OH}} = 3730\text{ cm}^{-1}$). A decrease in the content of basic OH groups necessary for the anchoring of chloride platinum complexes decreased the adsorptivity of support with respect to [PtCl₆]²⁻. The adsorption isotherms of H₂[PtCl₆] on the support pretreated at different temperatures (Fig. 6) demonstrate that the difference in adsorptivity can be quite high (more than a twofold), and calcination restoring the oxide phase cannot restore the relative content of functional groups of the surface and its adsorption properties in aqueous solutions. The presented experimental data illustrate that conclusions on the state of the surface obtained by FTIR spectroscopy can reflect and explain the processes occurring at the solid-liquid interface, i.e. under real conditions of the catalyst synthesis.

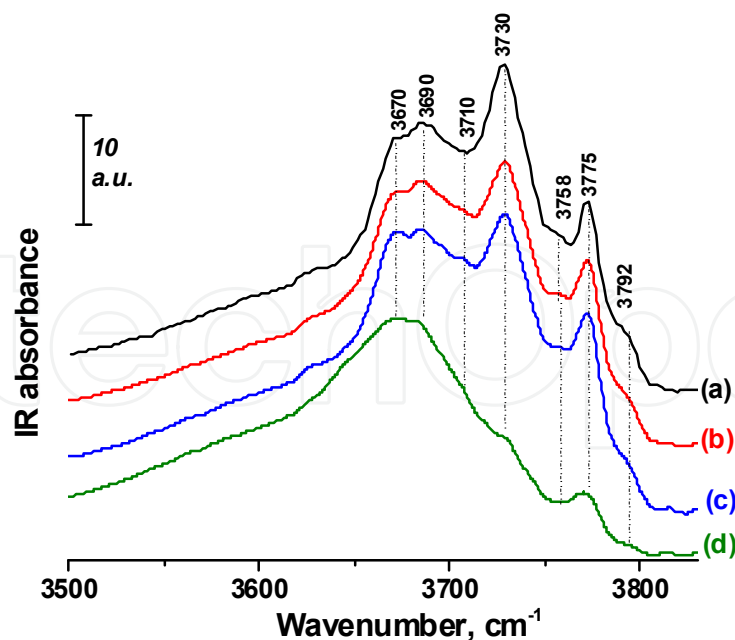


Fig. 5. FTIR spectra of hydroxyl cover of γ -Al₂O₃ (a) and γ -Al₂O₃ after hydrothermal treatment for 3 h at 150 (b), 180 (c) and 200 °C (d). The samples were calcined and outgassed at 500 °C

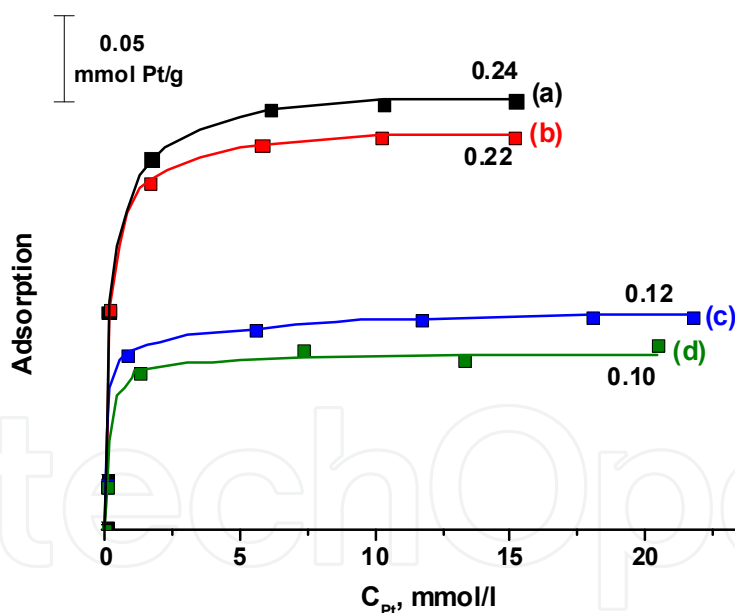


Fig. 6. Isotherms of H₂[PtCl₆] adsorption from aqueous solutions on γ -Al₂O₃ (a) and γ -Al₂O₃ after hydrothermal treatment for 3 h at 150 (b), 180 (c) and 200 °C (d) followed by heat treatment at 550 °C

Analysis of the FTIR spectra of adsorbed CO shows (Table 2) that introduction of the hydrothermal treatment step increases the concentration of all Lewis acid site types: weak (2180 and 2190 cm⁻¹), medium strength (2205 cm⁻¹), and strong (2225 cm⁻¹). The obtained result is important for application of this modifying method in the synthesis of catalytic compositions for the reactions requiring the presence of acid sites.

Thus, the FTIR spectroscopy study demonstrated that the main effect of the proposed method for modifying of the alumina surface consists in changing the ratio of different type sites capable of anchoring the active component precursor, in particular, in diminishing the fraction of more basic OH groups capable of coordination binding of the complexes (the formation of inner sphere complexes). The conclusions based on FTIR spectroscopy data and concerning changes in the surface state able to affect the mechanisms of precursor-support interaction and strength of such interaction were supported by independent ^{195}Pt NMR study. ^{195}Pt MAS NMR can be used to acquire data on the composition of adsorbed complexes and their interaction with the surface (Shelimov et al., 1999, 2000). Among advantages of this method for investigation of platinum complexes is a wide overall range of chemical shift (ca. 15000 ppm). This allows a relatively simple identification of Pt (IV) complexes with different structure from their ^{195}Pt chemical shift, which is very sensitive to the ligand environment. Thus, substitution of a Cl^- ligand in $[\text{PtCl}_6]^{2-}$ by H_2O or OH^- produces chemical shifts by 500 and 660 ppm, respectively.

However, in the study of complexes adsorbed on the support surface, the ^{195}Pt NMR signals are observed only if octahedral symmetry of the complexes is retained or slightly distorted during the adsorption. Coordination anchoring of a complex on alumina, when one or several chloride ligands of $[\text{PtCl}_6]^{2-}$ are substituted by hydroxyl groups of the support (see equation (8)), is accompanied by a substantial decrease in intensity and broadening of the peaks; sometimes NMR signals are not detected. Such situation is observed at the adsorption of complexes on the unmodified $\gamma\text{-Al}_2\text{O}_3$. At a maximum possible concentration of a metal complex for the chemisorption (platinum content of 4.5 wt%), the spectrum has only a broad peak with low intensity in the region characterizing $[\text{PtCl}_6]^{2-}$ (Fig. 7(a)).

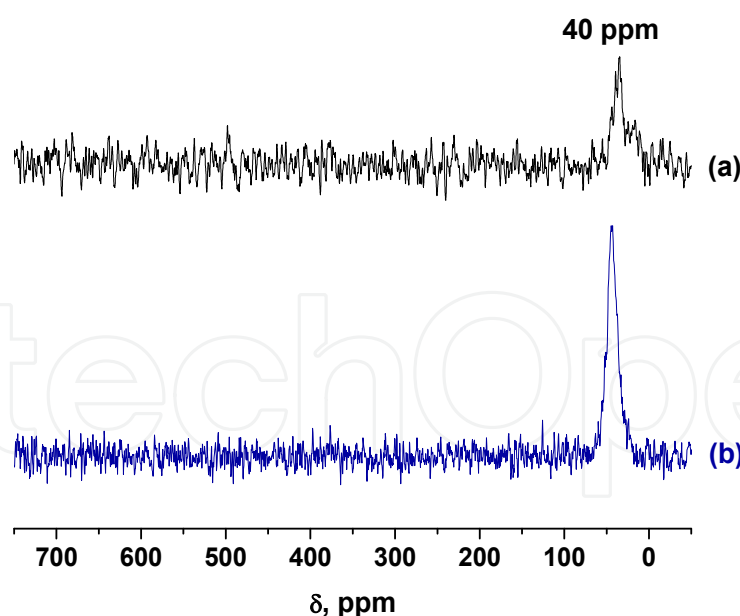


Fig. 7. ^{195}Pt MAS NMR spectra of 4.5%Pt/ $\gamma\text{-Al}_2\text{O}_3$ (unmodified support) (a) and 2.0%Pt/ Al_2O_3 with modified support (hydrothermal treatment at 180 °C, 3 h) (b)

This fact agrees with the diffuse reflectance electron spectroscopy and EXAFS examination of adsorbed complexes (Belskaya et al., 2008, 2011) showing that platinum on the $\gamma\text{-Al}_2\text{O}_3$ surface is mainly a component of the hydrolyzed coordinatively anchored complexes.

Meanwhile, in the case of modified support (Fig. 7(b)), there is an intense peak in the spectrum even at a two times lower platinum content corresponding to chloride complex $[\text{PtCl}_6]^{2-}$. Hence, anchoring of the complex does not produce noticeable changes in its chemical composition; moreover, there is a considerable decrease in the contribution of coordination binding with the surface involving OH groups of the support. Electrostatic interaction of a metal complex with the modified support with respect to equation (7) seems to prevail here. In addition, temperature-programmed reduction followed by chemisorption of H_2 and CO probe molecules was used to confirm that a decrease in the bond strength between precursor and support decreases the reduction temperature of adsorbed platinum species and diminishes the dispersion of supported particles by a factor of more than 3.

3.1.2.3 The effect of $\gamma\text{-Al}_2\text{O}_3$ modifying with silica on acid-base properties of the surface

Due to its high thermal stability, alumina modified with silica is a promising support for exhaust neutralization catalysts. Acid-base properties of the developed composition can be optimized by means of FTIR spectroscopy of adsorbed probe molecules. Composition of the support was varied by changing the silica concentration from 1.5 to 10 wt%. The modifying SiO_2 compound was formed in the pore space of $\gamma\text{-Al}_2\text{O}_3$ support during thermal decomposition of preliminarily introduced tetraethoxysilane $\text{Si}(\text{OC}_2\text{H}_5)_4$.

Figure 8 shows FTIR spectra in the region of OH group stretching vibrations of the aluminum oxide samples modified with silica in comparison with the spectrum of initial $\gamma\text{-Al}_2\text{O}_3$. The spectra of all modified oxides show a decrease in intensity of absorption bands corresponding to OH groups of the bridging and terminal types as compared to initial $\gamma\text{-Al}_2\text{O}_3$. The additional absorption bands appear at 3740-3745 cm^{-1} , their intensity growing with silicon content of the sample. The band at 3745 cm^{-1} can be assigned to the terminal $\text{Si}(\text{OH})$ groups.

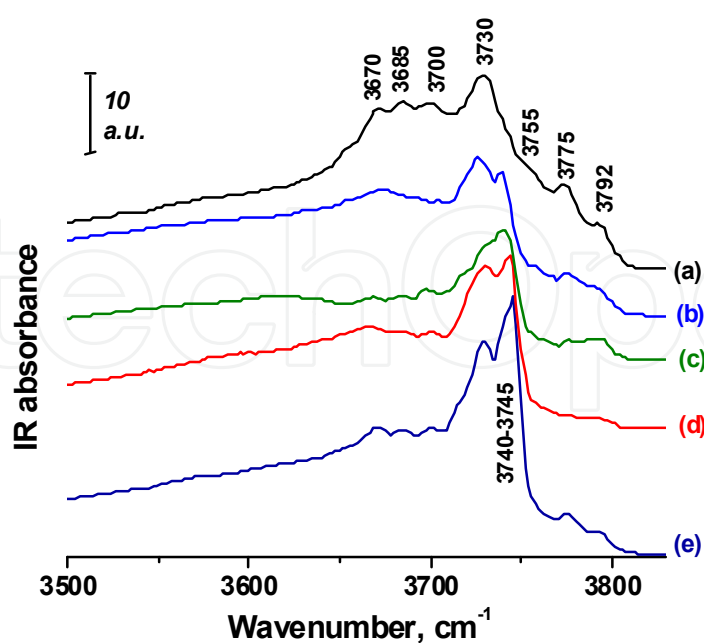


Fig. 8. FTIR spectra of hydroxyl groups for $\gamma\text{-Al}_2\text{O}_3$ calcined at 550 °C (a) and of 1.5% $\text{SiO}_2/\gamma\text{-Al}_2\text{O}_3$ (b), 5% $\text{SiO}_2/\gamma\text{-Al}_2\text{O}_3$ (c), 7% $\text{SiO}_2/\gamma\text{-Al}_2\text{O}_3$ (d), 10% $\text{SiO}_2/\gamma\text{-Al}_2\text{O}_3$ (e) calcined at 450 °C. The samples were outgassed at 450 °C

Adsorption of CO on $\gamma\text{-Al}_2\text{O}_3$ at $-196\text{ }^\circ\text{C}$ results in the shift of OH bands with ν_{OH} 3700 and 3775 cm^{-1} to the lower frequency region due to perturbation of OH stretch by hydrogen bonding. Aluminum oxides have no Brønsted acidity according to the minor shift of OH stretching vibration ($\Delta\nu_{\text{OH/CO}}$) by $120\text{-}130\text{ cm}^{-1}$ (Maache et al., 1993; Paze et al., 1997). A large shift of OH stretching vibrations for the silicon-containing samples with $\Delta\nu_{\text{OH/CO}}$ equal to $240\text{-}290\text{ cm}^{-1}$ indicates the formation of strong Brønsted acid sites on the sample surface. As demonstrated by Crépeau et al. (Crépeau et al., 2006), high acidity for amorphous silica-alumina can be shown by free silanol groups located nearby an Al atom. Acidity of OH groups at 3740 cm^{-1} of the $10\%\text{ SiO}_2/\text{Al}_2\text{O}_3$ sample approaches the acidity of bridged $\text{Si}(\text{OH})\text{Al}$ groups in zeolites with the band at 3610 cm^{-1} according to the value of the low frequency shift of OH vibrations with adsorbed CO ($\Delta\nu_{\text{OH/CO}} = 300\text{ cm}^{-1}$).

For all tested systems, the spectrum of adsorbed CO has a.b. with $\nu_{\text{CO}} = 2158\text{-}2163\text{ cm}^{-1}$ attributed to CO hydrogen-bonded with hydroxyl groups, and a.b. with $\nu_{\text{CO}} = 2130\text{-}2135\text{ cm}^{-1}$ related with absorption of physisorbed CO. Besides, for all silicon-containing systems, there is a.b. with $\nu_{\text{CO}} \approx 2170\text{ cm}^{-1}$, which was assigned to CO hydrogen-bonded with Brønsted acid sites. Concentrations of these sites estimated from the intensity of a.b. with $\nu_{\text{CO}} \approx 2170\text{ cm}^{-1}$ are listed in Table 4. One may see that concentration of Brønsted sites increases with the silica content in the sample.

Sample	Specific surface area, m^2/g	$\Delta\nu_{\text{OH}}, \text{cm}^{-1}$	Concentration of Brønsted acid sites, $\mu\text{mol/g}$
$\gamma\text{-Al}_2\text{O}_3$	162	120-130	-
1.5% $\text{SiO}_2/\text{Al}_2\text{O}_3$	120	240	14
5% $\text{SiO}_2/\text{Al}_2\text{O}_3$	131	240	28
7% $\text{SiO}_2/\text{Al}_2\text{O}_3$	179	240	30
10% $\text{SiO}_2/\text{Al}_2\text{O}_3$	191	290	33

Table 4. Surface concentrations of Brønsted acid sites and specific surface area of silica promoted aluminum oxides

By using low-temperature CO adsorption, the concentration and strength of coordinatively unsaturated surface sites of the synthesized oxide systems were also estimated. The absorption bands and their intensities observed in the spectrum of $\gamma\text{-Al}_2\text{O}_3$ calcined at $550\text{ }^\circ\text{C}$ (Table 5) are close to those reported in the previous Sections. Minor distinctions are related with the preparation procedures and texture characteristics of $\gamma\text{-Al}_2\text{O}_3$. The types of Lewis acid sites identified by CO adsorption on the surface of silicon-containing systems are close to the types of Lewis acid sites for $\gamma\text{-Al}_2\text{O}_3$. The concentration of super strong Lewis acid sites ($Q_{\text{CO}} = 59.5\text{ kJ/mol}$) decreases, whereas the concentration of strong Lewis acid sites ($Q_{\text{CO}} = 54\text{ kJ/mol}$) and medium strength Lewis acid sites ($Q_{\text{CO}} = 42.5\text{ kJ/mol}$) increases. The type of Lewis acid sites with $\nu_{\text{CO}} \approx 2230\text{ cm}^{-1}$ is typical of aluminosilicate structures and can be assigned to aluminum in a defect octahedral coordination, which is bonded to silicon atom in the second coordination sphere (Paukshtis, 1992).

Four types of base sites were identified on the alumina surface using deuteriochloroform as a probe molecule. The spectra are shown in Fig. 9; site strengths and concentrations are listed

Type of Lewis acid site	Super strong	Strong	Medium I	Medium II	Weak
ν_{CO} , cm^{-1}	2240	2230	2220	2205	2190
Q_{CO} , kJ/mol	59.5	54	48.5	42.5	33
Samples	Concentration, $\mu\text{mol/g}$				
$\gamma\text{-Al}_2\text{O}_3$	0.4	1	8	6	300
1.5% $\text{SiO}_2/\text{Al}_2\text{O}_3$	0.3	5	4	22	330
5% $\text{SiO}_2/\text{Al}_2\text{O}_3$	-	6	4	15	290
7% $\text{SiO}_2/\text{Al}_2\text{O}_3$	-	7	4	18	300
10% $\text{SiO}_2/\text{Al}_2\text{O}_3$	-	12	4	17	320

Table 5. Types and concentrations of Lewis acid sites according to FTIR spectroscopy of adsorbed CO

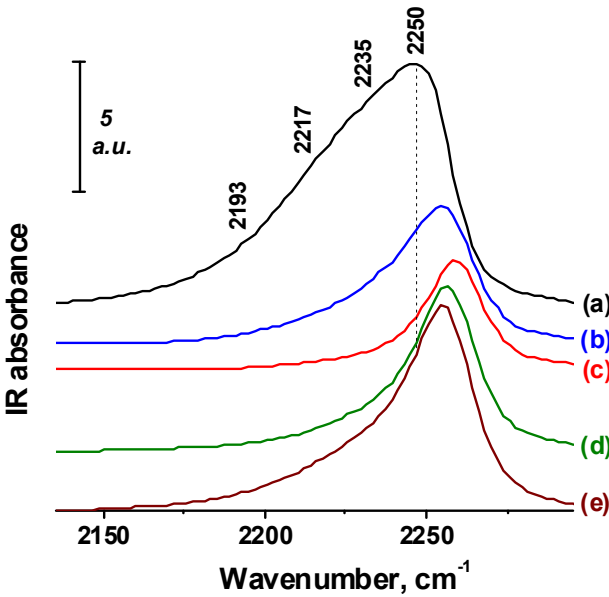


Fig. 9. FTIR spectra of adsorbed deuteriochloroform on $\gamma\text{-Al}_2\text{O}_3$ (a) and aluminum oxides modified with 1.5% (b), 5% (c), 7% (d), and 10% (e) of SiO_2

in Table 6. Strong base sites of alumina are characterized by a.b. with ν_{CD} 2193 and 2217 cm^{-1} , which correspond to the calculated PA values of 942 and 915 kJ/mol . The band at 2235 cm^{-1} corresponds to medium-strength base sites, whereas the band at 2250 cm^{-1} is attributed to weak base sites. Paukshtis (Paukshtis, 1992) hypothesized that the strong and medium-strength base sites are bridging oxygen atoms (Al-O-Al), whereas the weak sites are oxygen atoms of OH groups (Al-OH). The introduction of 1.5-5% SiO_2 results in disappearance of super strong base sites and an abrupt decrease in the concentration of other types of base sites, which can be related with sequential blocking of the surface by silica. The introduction of 7-10% SiO_2 increases the concentration of strong and medium strength base sites, which evidences the formation of a new surface phase, probably aluminosilicate one. This phase blocks only partially the surface of initial alumina. All the samples modified with silica have high-frequency a.b. of adsorbed deuteriochloroform at 2255-2258 cm^{-1} characterizing the sites which basicity is close to that of silica gel OH groups.

Type of base site	Super strong	Strong	Medium	Weak I	Weak II
$\Delta\nu_{CD}$, cm ⁻¹	72	48-43	30-23	15	10-7
PA, kJ/mol	942	915-908	885-857	839	
Samples	Concentration, $\mu\text{mol/g}$				
$\gamma\text{-Al}_2\text{O}_3$	48	130	163	210	
1.5% SiO ₂ /Al ₂ O ₃	-	38	74	-	570*
5% SiO ₂ /Al ₂ O ₃	-	-	21	-	560*
7% SiO ₂ /Al ₂ O ₃	-	26	56	-	730*
10% SiO ₂ /Al ₂ O ₃	-	80	124	-	700*

Table 6. Types and concentrations of base sites according to FTIR spectroscopy of adsorbed CDCl₃. * The concentration may be overrated due to close proximity of the band of adsorbed and physisorbed deuteriochloroform

Thus, Section 3.1 demonstrated the conventional approaches employed in FTIR spectroscopy for investigation of functional groups on the alumina surface. Original methods for modifying of this most popular support were reported. Applicability of FTIR spectroscopy for estimating the effect of modifying on the surface acid-base properties and optimizing the composition of surface sites was shown. Thus, FTIR spectroscopy in combination with other methods can explain changes in adsorption and catalytic characteristics and predict the behavior of oxide surface under real conditions of catalyst synthesis and testing.

3.2 State of palladium in Pd/SZ catalysts

Sulfated zirconia (SZ) promoted with noble metals is a very effective catalyst for isomerization of alkanes due to its high activity at low temperatures and high selectivity of isomers formation (Song & Sayari, 1996). Information on the state of metal in isomerization catalyst is quite topical. For example, metallic platinum or palladium improve the dehydrogenating capacity of the catalyst, which affects the formation of isoalkanes and enhance the production of atomic hydrogen which is necessary for the removal of coke precursors (Vera et al., 2002, 2003). It should be noted that state of the metal is determined to a great extent by the conditions of oxidative and reductive treatment of catalysts before the reaction. Thus, the challenge is to find the optimal pretreatment temperatures allowing the formation of acid sites and retaining the metallic function.

A convenient method for solving this problem is FTIR spectroscopy of adsorbed CO molecules. In our earlier work (Belskaya et al., 2010), this method was used for studying the state of supported palladium particles in Pd/SZ under different conditions of catalyst pretreatment. In the experiment, the catalyst treatment in various gas media (air, hydrogen) and at different temperatures (100-400 °C) was performed directly in a spectrometer cell. CO adsorption was carried out over a pressure range of 0.1 to 10 mbar at room temperature.

IR spectra of CO adsorbed on the surface of Pd/SZ pretreated under different conditions are shown in Fig. 10. The spectrum of CO adsorbed on the sample that was activated in air shows several a.b. located at 1935, 2030, 2090, 2125, 2150, 2170 and 2198 cm⁻¹ (Fig. 10(a)). The

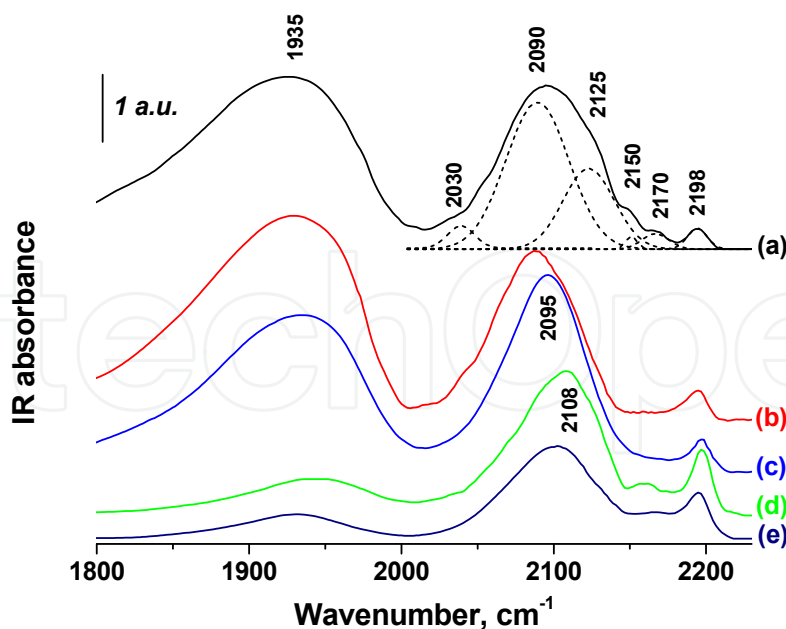


Fig. 10. FTIR spectra of CO adsorbed on Pd/SZ (25 °C; 10 mbar) after oxidation in air at 400 °C (a), after reduction in hydrogen at 150 °C (b), 200 °C (c), 300 °C (d) and 350 °C (e). All spectra are background subtracted. Spectra were offset for clarity

sharp band at 2090 cm^{-1} and the broad band around 1935 cm^{-1} are ascribed to terminal and bridge-coordinated CO on Pd^0 , respectively (Sheppard & Nguyen, 1978). The bands at 2030, 2125 and 2150 cm^{-1} can be attributed, respectively, to bridged CO complex with Pd^+ and linear CO complexes with Pd^+ and Pd^{2+} isolated ions; the band at 2170 cm^{-1} can be assigned to CO linearly adsorbed on Pd^{2+} in PdO species (Hadjiivanov & Vayssilov, 2002). Besides, the band at 2196–2198 cm^{-1} is present in all spectra and may be assigned to CO adsorption on Zr^{4+} ions (Morterra et al., 1993). The highest intensity of this a.b. is observed for the sample reduced in H_2 at 300 °C. This fact confirms studies concerning the necessity of high-temperature reduction of SZ to obtain the greatest Lewis acidity of the catalyst after metal incorporation.

According to FTIR spectroscopy data, in oxidized Pd/SZ sample a part of palladium is presented as Pd^0 (high intensities of a.b. at 1935 and 2090 cm^{-1}). Supposedly, the formation of metallic palladium can be caused by evacuation at high temperatures during the pretreatment in IR cell. This assumption was confirmed in a special experiment by means of UV-vis spectroscopy (Belskaya et al., 2010). Pd/SZ catalyst after the oxidation is characterized by a.b. at 20500, 34000, 39500 and 46000 cm^{-1} . The a.b. at 20500 and 39500 cm^{-1} can be attributed, respectively, to d-d transition and ligand-to-metal charge transfer of Pd^{2+} ions in D_{4h} oxygen environment (Rakai et al., 1992). Evacuation at 300 °C decreases the concentration of Pd^{2+} ions in PdO (a decrease in the intensity of a.b. at 20500 cm^{-1} was observed). This experiment clearly demonstrates that a possible effect of pretreatment conditions on the state of catalyst surface in IR spectroscopy study (in this case, the effect of evacuation at elevated temperatures) should be taken into account.

In the FTIR spectra of CO adsorbed on Pd/SZ samples that were reduced at 150–200 °C (Fig. 10(b), (c)), the a.b. at 1930 and 2090–2095 cm^{-1} attributed to metallic palladium dominate. Bands at 2125–2170 cm^{-1} , assigned to CO adsorbed on oxidized Pd ions, almost

vanish. The differences between spectra of adsorbed CO on Pd/SZ samples reduced at 200 and 300–350 °C are dramatic (Fig. 10(c)–(e)). An increase in the reduction temperature suppresses the bridge coordinated CO IR bands, decreases the intensity and slightly shifts the stretching frequency of linearly adsorbed CO to higher wavenumbers. Such shift occurs when CO is chemisorbed on the sulfur-saturated Pd surface (Guerra, 1969; Jorgensen & Madix, 1985). So, appearance of the band at 2105–2108 cm^{-1} can be attributed to linear CO complexes with palladium in an electron-deficient state with high S-coverage. According to (Jorgensen & Madix, 1985; Ivanov & Kustov, 1998) a possible reason for the decrease in concentration of bridging CO is the partial covering of Pd surface by sulfur species. Thus, we suppose that low CO chemisorption capacity of Pd^0 atoms in Pd/SZ samples reduced at high temperatures is due to partial sulfur coating of the metal surface. Therewith, new a.b. at 2135 and 2160 cm^{-1} are observed in the spectra of CO adsorbed on Pd/SZ samples that were reduced at 300–350 °C. These bands appear on admission of 0.1 mbar CO and grow in intensity with increasing CO pressure (Belskaya et al., 2010); they are attributed to CO complexes with oxidized Pd^+ and Pd^{2+} species, probably in $\text{Pd}^{n+}\text{-S}^{2-}$ sites (Vazquez-Zavala et al., 1994).

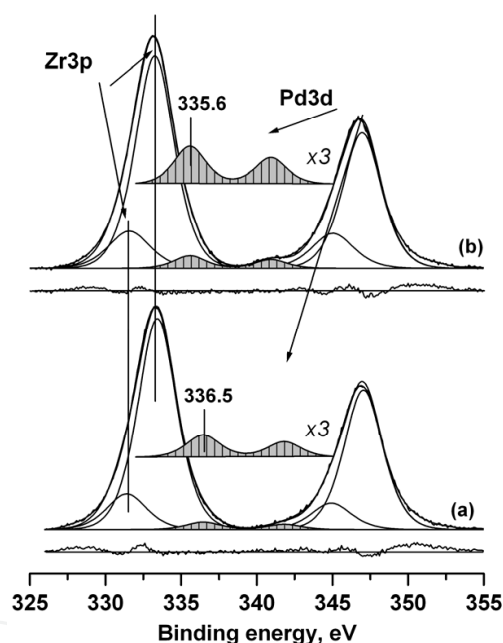


Fig. 11. Zr3p and Pd3d core-level spectra of the samples after oxidation in air at 400 °C (a) and after reduction in hydrogen at 300 °C (b). For clear identification, Pd3d spectra are multiplied by 3

IR spectroscopic data on the state of supported palladium in Pd/SZ after oxidation and reduction were compared with X-ray photoelectron spectroscopy (XPS) data for the same samples. Figure 11 shows the X-ray photoelectron spectra in the spectral region of Zr3p and Pd3d core-level lines. The difference curves between experimental spectrum and the envelope of the fit are presented under each spectrum. After calcination in air at 400 °C (Fig. 11(a)), palladium spectrum can be described by one doublet line with binding energy (E_b) of $\text{Pd3d}_{5/2}$ 336.5 eV. Such value of E_b is close to that for the oxidized palladium species in palladium oxide PdO (Brun et al., 1999; Pillo et al., 1997). After the action of H_2 (Fig. 11(b)), Pd3d spectrum gives a peak with E_b ($\text{Pd3d}_{5/2}$) 335.6 eV, which is assigned to

small metal particles. Bulk metal palladium is known to have E_b of $Pd3d_{5/2}$ at 335.2 eV (Brun et al., 1999; Otto et al., 1992). In our case, a small increase of E_b is likely to originate from the size effect (Mason, 1983). The formation of bulk palladium sulfide was not observed because the corresponding value of E_b of $Pd3d_{5/2}$, which is about 337.2 eV (Chaplin et al., 2007), was not detected. Thus, changes of the metal surface after high temperature reduction in the H_2 atmosphere, which are demonstrated by the FTIR spectra, have no significant effect on the electronic state of metal particles: according to XPS data, Pd remains in the metallic state. H_2S resulting from sulfate reduction blocks the active metal surface, most likely without formation of PdS in large amounts. However, it cannot be unambiguously concluded from Pd3d and S2p core-level spectra whether the sulfide film forms on the palladium surface after reduction or not.

For assessment of the state of palladium, we also used a model reaction which is commonly employed to test the metallic function of catalysts – low-temperature (50–90 °C) hydrogenation of benzene. There was a clear effect of pretreatment conditions on the conversion of benzene to cyclohexane. Pd/SZ catalyst reduced at the temperature corresponding to metal formation (according to TPR data) demonstrated the highest conversion. In the case of reduction temperature above 120 °C, before the catalytic test H_2S was detected in the exhaust gases, and poisoning of the metal function was observed. Thus, in Pd/SZ catalysts, after the reduction treatment at 300 °C, hydrogenation activity of palladium is strongly inhibited. However, the constant activation energy and complete recovery of hydrogenation activity under mild regeneration conditions (Belskaya et al., 2010) indicate that the metal surface is only blocked by sulfate decomposition products without their chemical interaction with palladium.

Thus, FTIR spectroscopy of adsorbed CO used to examine the state of supported palladium in Pd/SZ catalysts provided data that agree well with the data obtained by independent methods – XPS and a model reaction for testing the metal function. Analysis of changes in the state of surface revealed by FTIR spectroscopy can be useful for explaining the adsorption and catalytic properties as well as for optimizing the conditions of thermal stages during catalyst synthesis.

3.3 Alumina promoted Pt/SO_4^{2-} - ZrO_2

The approaches for controlling the SO_4^{2-} - ZrO_2 acidity are of great practical importance, as they can change the catalyst activity and selectivity in various acid-catalyzed reactions (Hua et al., 2000; Lavrenov et al., 2007; Zalewski et al., 1999). In our works (Kazakov et al., 2010, 2011, 2012), we optimized the acidic and hydrogenation properties of bifunctional Pt/SO_4^{2-} - ZrO_2 catalyst for the one-step hydroisomerization of benzene-containing fractions, which is intended for elimination of benzene in gasoline while minimizing the octane loss. The introduction of alumina into the catalyst was suggested as the main modifying procedure. IR spectroscopy allowed us to elucidate the effect of catalyst composition on the properties of surface functional groups, to reveal the role of alumina in the formation of metal and acid sites, and provided a detailed characterization of the surface properties of optimal hydroisomerization catalyst. The work was performed with catalysts Pt/SO_4^{2-} - ZrO_2 (4.5 wt% SO_4^{2-}), Pt/SO_4^{2-} - ZrO_2 - Al_2O_3 , (3.1 wt% SO_4^{2-} and 67.8 wt% Al_2O_3) and Pt/Al_2O_3 . Samples were denoted as Pt/SZ, Pt/SZA and Pt/A, respectively. Platinum concentration was 0.3 wt%. We studied also the supports used for the catalyst synthesis (SZ, SZA and A,

respectively). The preparation procedure for supports and catalysts is reported in (Kazakov et al., 2010, 2011).

3.3.1 The effect of alumina introduction on the state of supported platinum

The formation of platinum sites and the state of metal in a finished catalyst strongly depend on the interaction of precursor with the surface groups of support. As it was shown earlier, the composition and amount of hydroxyl groups on the support surface play a significant role in the platinum compounds anchoring from a solution of $H_2[PtCl_6]$. Infrared spectra of the OH stretching region for SZ, SZA and A supports are shown in Fig. 12. The spectrum of sample SZ is represented by a.b. at 3651 cm^{-1} , which corresponds to bridging OH groups with acidic properties (Kustov et al., 1994; Manoilova et al., 2007). The FTIR spectrum of SZA sample has a.b. at 3772 and 3789 cm^{-1} assigned to terminal OH groups, and a.b. 3677 and 3728 cm^{-1} corresponding to bridging OH groups (Knözinger & Ratnasamy, 1978). The presence of these types of OH groups is typical for the $\gamma\text{-Al}_2\text{O}_3$ surface (sample A in Fig. 12).

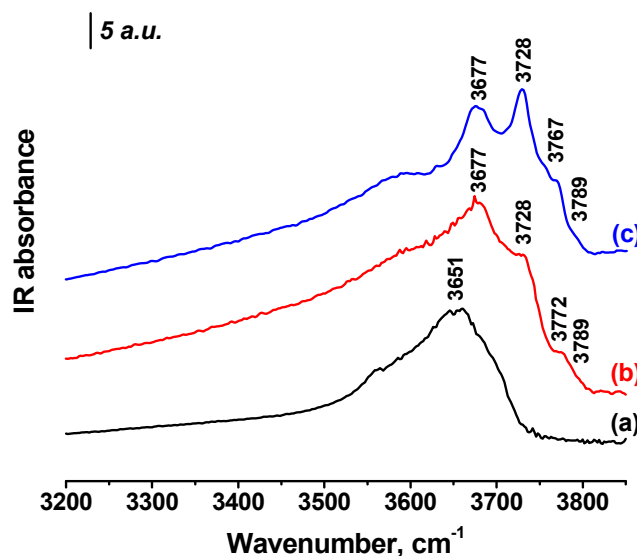


Fig. 12. FTIR spectra of the catalyst supports in the OH stretching region: SZ (a), SZA (b), A (c). Spectra were offset for clarity. Prior to recording, the samples were evacuated at $400\text{ }^{\circ}\text{C}$

Significant distinctions in the hydroxyl cover suggest different mechanisms of the interaction between metal complex and support. Indeed, the presence of only the hydroxyl groups with acidic properties on the SZ surface explains the absence of chemisorption anchoring of the anionic $[PtCl_6]^{2-}$ complex. After the introduction of 67.8 wt% alumina into sulfated zirconia sites for chloroplatinate ions sorption appear on the surface of mixed $SO_4^{2-}\text{-ZrO}_2\text{-Al}_2\text{O}_3$ support. However, the concentration of bridging $Al^{VI}(\text{OH})Al^{VI}$ groups (3728 cm^{-1}) that are most active in chloroplatinate anchoring, and terminal groups (3772 and 3789 cm^{-1}) on SZA support is lower than their concentration on the alumina surface, which causes a smaller fraction of complexes anchored by chemisorption (81% for SZA and 100% for A).

The reduction temperature of platinum species anchored on SZA support, which characterizes the strength of precursor – support interaction, also has a medium value.

According to TPR data, platinum reduction on SZ surface (sample Pt/SZ) in the absence of chemisorption interaction starts from 90 °C. However, in the samples with alumina this process shifts toward higher temperatures, and a maximum rate of hydrogen consumption is observed at 210 and 225 °C for Pt/SZA and Pt/A.

The state of supported platinum in finished catalysts after reduction in hydrogen was investigated by FTIR spectroscopy of adsorbed CO (Fig. 13). The band with ν_{CO} 2200-2208 cm^{-1} , which is present in all the spectra, corresponds to CO complexes with Lewis acid sites of the catalysts (Morterra et al., 1993). The spectrum of Pt/A sample shows a.b. with ν_{CO} 2065 cm^{-1} corresponding to stretching vibrations of CO linearly adsorbed on Pt^0 , and a broad band at 1830 cm^{-1} characterizing the bridging CO species on Pt^0 (Apesteguia et al., 1984; Kooh et al., 1991). After CO adsorption on Pt/SZ, there appear bands at 2100 and 2150 cm^{-1} , which have close intensities and correspond to linear CO complexes with Pt^0 and $\text{Pt}^{\delta+}$, respectively (Grau et al., 2004; Morterra et al., 1997). In the case of Pt/SZA, the frequencies of CO (a.b. 2085 cm^{-1}) adsorbed on metal platinum particles are intermediate in comparison with frequencies for samples Pt/A and Pt/SZ.

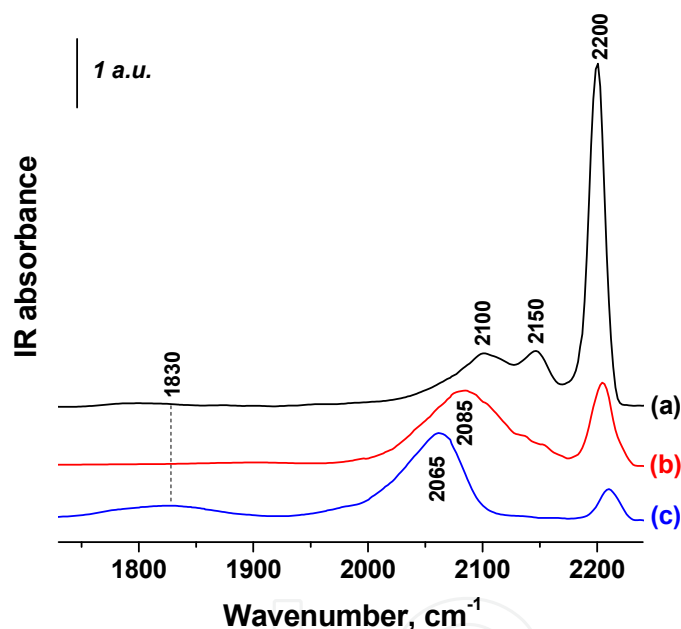


Fig. 13. FTIR spectra of CO (25 °C; 10 mbar) adsorbed on the catalysts: Pt/SZ (a), Pt/SZA (b), Pt/A (c). Prior to recording, the samples were reduced in hydrogen flow at 300 °C and then evacuated at 500 °C

In comparison with Pt/SZ, the band corresponding to CO - Pt^0 complexes for samples Pt/SZA and Pt/SZ is shifted toward higher frequencies by 20 and 35 cm^{-1} , respectively. Such upward shift of ν_{CO} was also observed for Pd/SZ samples (Section 3.2) and can be related to the presence of sulfur species on the metal surface (Apesteguia et al., 1984, 1987; J.R. Chang & S.L. Chang, 1998). These sulfur species are formed both at the stage of oxidative treatment and during the reduction; they can poison the metal partially or completely (Dicko et al., 1994; Iglesia et al., 1993). As a result, Pt/SZ demonstrates very poor hydrogenation activity and does not chemisorb hydrogen (Table 7). Pt/SZA sample has an enhanced hydrogenation activity in comparison with Pt/SZ; nevertheless, it is lower than that observed for Pt/A.

Catalyst	H/Pt	Benzene conversion, %
Pt/SZ	0.00	1.8
Pt/SZA	0.44	40.7
Pt/A	0.85	97.1

Table 7. Hydrogen chemisorption and benzene hydrogenation over Pt/SZ, Pt/SZA and Pt/A catalysts. Benzene hydrogenation conditions: 200 °C, 0.1 MPa, weight hourly space velocity 4.0 h⁻¹, H₂ : C₆H₆ molar ratio 8

The increasing accessibility of platinum sites for adsorption and catalytic reaction in a series Pt/SZ < Pt/SZA < Pt/A can be attributed both to a decrease in the content of sulfur compounds in the catalyst upon dilution of sulfated zirconia with alumina, and to a higher resistance to poisoning of more disperse supported platinum crystallites produced by chemisorption anchoring of a precursor (J.R. Chang et al., 1997).

3.3.2 The effect of alumina introduction on the acidic properties of Pt/SO₄²⁻-ZrO₂

The strength and concentration of acid sites of catalysts Pt/SZ, Pt/SZA and Pt/A reduced at 300 °C were estimated from FTIR spectra of adsorbed CO and pyridine molecules. After CO adsorption, spectra of all the samples had the a.b. 2180-2208 cm⁻¹ corresponding to CO complexes with Lewis acid sites of different strength, a.b. 2168-2171 cm⁻¹ assigned to CO complexes with Brønsted acid sites, a.b. 2160-2162 cm⁻¹ characterizing CO complexes with hydroxyl groups having weak acidic properties, and a.b. 2133-2148 cm⁻¹ corresponding to the adsorption of physisorbed CO molecules. In all cases, only the medium strength (a.b. with ν_{CO} 2204-2208 cm⁻¹ for Pt/SZ, 2202-2208 cm⁻¹ for Pt/SZA, and 2204 cm⁻¹ for Pt/A) and weak Lewis acid sites (a.b. with ν_{CO} 2194, 2188, 2180 cm⁻¹ for Pt/SZ, and 2192 cm⁻¹ for Pt/SZA and Pt/A) were detected. After the pyridine adsorption, we observed a.b. corresponding to complexes of pyridine molecules with Brønsted acid sites (1544 cm⁻¹) and Lewis acid sites (1445 cm⁻¹).

Data on the concentration of Lewis acid sites (calculated from the integral intensities of adsorbed CO a.b.) and Brønsted acid sites (calculated from the integral intensities of adsorbed pyridine a.b.) for the tested catalysts are listed in Table 8. The Pt/SZ catalyst has the highest content both of Lewis and Brønsted acid sites. For sample Pt/A, Brønsted acid sites able to protonate pyridine were not observed. Pt/SZA has intermediate position with respect to its acidic properties. The Brønsted acid sites content in this sample is 3.5 times lower as compared to Pt/SZ, which virtually corresponds to a decrease of ZrO₂ amount in its composition (29.1 against 95.5 wt%, respectively). The total amount of Lewis acid sites in comparison with Pt/SZ decreases twofold. However, the ratio of medium strength and weak Lewis acid sites for Pt/SZA sample corresponds to the ratio revealed for Pt/SZ. Thus, the introduction of alumina into Pt/SZ system decreases the amount of Lewis and Brønsted acid sites, which is related to the effect of its dilution with a component having a lower intrinsic acidity. The observed nonadditive change in the concentration of acid sites, in particular Lewis acid sites, may be caused by interaction of the system components, which was noted earlier (Kazakov et al., 2010).

Catalyst	ν_{CO} , cm ⁻¹	Lewis acid sites, $\mu\text{mol/g}$	Lewis acid sites, $\mu\text{mol/g}$		Total Lewis acid sites, $\mu\text{mol/g}$	Total Brønsted acid sites, $\mu\text{mol/g}$
			medium	weak		
Pt/SZ	2208	25	115	530	645	32
	2204	90				
	2194	260				
	2188	240				
	2180	30				
Pt/SZA	2208	15	60	250	310	9
	2202	45				
	2192	250				
Pt/A	2204	29	29	350	379	0
	2192	350				

Table 8. Acidic properties of Pt/SZ, Pt/SZA and Pt/ A catalysts according to FTIR spectroscopy of adsorbed CO and pyridine. Prior to recording, samples were reduced in hydrogen flow at 300 °C and then evacuated at 500 °C

Results of FTIR spectroscopic study are in good agreement with the model acid-catalyzed reactions of n-heptane and cyclohexane isomerization. The introduction of alumina into Pt/SZ decreases the total catalyst activity in n-C₇H₁₆ isomerization, which shows up as increase of the temperature of 50% n-heptane conversion from 112 to 266 °C (Table 9). For isomerization of cyclohexane to methylcyclopentane, higher operating temperatures are thermodynamically more favorable (Tsai et al., 2011). As a result, Pt/SZA catalyst is more efficient for cyclohexane isomerization due to higher selectivity at higher temperatures (Table 10).

Catalyst	X n-C ₇ , %	t, °C	Iso-C ₇ yield, %	Selectivity to iso-C ₇ , %
Pt/SZ	50.0	112	43.3	86.5
Pt/SZA	50.0	266	47.1	94.2
Pt/A	12.9	300	6.3	47.0

Table 9. Isomerization of n-heptane over Pt/SZ, Pt/SZA and Pt/ A catalysts. Reaction conditions: 1.5 MPa, weight hourly space velocity 4.0 h⁻¹, H₂ : n-C₇H₁₆ molar ratio 5. X - conversion

Catalyst	200 °C			275 °C		
	X CH, %	MCP yield, %	Selectivity to MCP, %	X CH, %	MCP yield, %	Selectivity to MCP, %
Pt/SZ	70.0	57.1	81.7	91.8	26.2	29.6
Pt/SZA	4.4	4.4	99.3	74.4	69.6	93.7
Pt/A	-	-	-	0.2	0.0	-

Table 10. Isomerization of cyclohexane over Pt/SZ, Pt/SZA and Pt/ A catalysts. Reaction conditions: 1.5 MPa, weight hourly space velocity 4.0 h⁻¹, H₂ : C₆H₁₂ molar ratio 5. X - conversion; CH - cyclohexane; MCP - methylcyclopentane

Thus, FTIR spectroscopy applied to investigation of Pt/SZA system proved to be a highly informative method, which allowed us to elucidate the role of alumina both in the formation of platinum sites and in the catalyst behavior in the acid-catalyzed reactions. Although state of the surface under conditions of FTIR spectroscopic examination strongly differ from its state upon contacting with aqueous solutions of metal complexes or in catalytic reactions, FTIR spectroscopy data on the state of supported platinum as well as on the nature and strength of acid sites can be used to optimize the composition of bifunctional catalyst Pt/SZA designed for hydroisomerization of benzene-containing fractions.

4. Conclusion

The possibilities of FTIR spectroscopy, in particular with the use of adsorbed CO, pyridine or deuteriochloroform probe molecules, for investigation of some model and industrially important supports and catalysts were demonstrated. The effect of chemical composition of a support (Al_2O_3 , $\text{Al}_2\text{O}_3\text{-SiO}_2$, $\text{SO}_4^{2-}\text{-ZrO}_2$, $\text{SO}_4^{2-}\text{-ZrO}_2\text{-Al}_2\text{O}_3$) and modification technique on the concentration and ratio of different types of OH groups and coordinatively unsaturated surface sites was shown.

Concentrations of the surface sites on supports before and after anchoring of the active metal component were compared to demonstrate a relation between composition of the functional surface groups, adsorption capacity of the support and strength of the interaction between metal complex precursor and support, and to identify the sites involved in anchoring of the active component. The impact of support nature and composition, conditions of oxidation and reduction treatments on the metal-support interaction and ratio of oxidized and reduced forms of supported metal (platinum or palladium) was revealed.

FTIR spectroscopy data for the examined catalytic systems were compared with the data of XPS, diffuse reflectance electron spectroscopy, H_2 and CO chemisorption for determination of supported metal dispersion, and temperature-programmed reduction as well as with the results of testing in the following catalytic reactions: double-bond isomerization of 1-hexene, hydrogenation of benzene and isomerization of n-heptane and cyclohexane.

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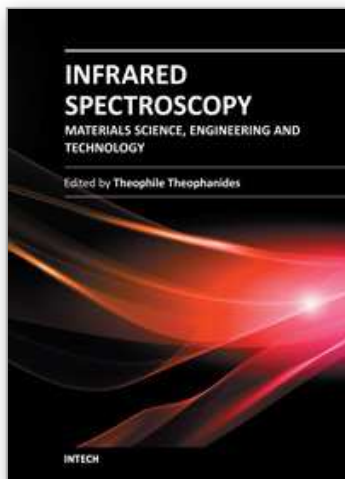
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